

On the exact treatment of Time Dependent Self-Interaction Correction

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Abstract

We present a new formulation of the time-dependent self-interaction correction (TD-SIC). It is derived variationally obeying explicitly the constraints on orthonormality of the occupied single-particle orbitals. The thus emerging rather involved symmetry condition amongst the orbitals is dealt with using two separate sets of (occupied) single-particle wavefunctions, related by a unitary transformation. The double-set TDSIC scheme is well suited for numerical implementation. We present results for laser-excited dynamics in a 1D model for a molecule and in fully fledged 3D calculations.

Key words: Time Dependent Density Functional Theory, Self-Interaction Correction, Irradiation

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1 Introduction

Density Functional Theory (DFT) [1,2,3,4] has become over the last decades a widely used theoretical tool for the description and analysis of electronic properties in physical and chemical systems. This applies particularly to systems with sizeable numbers of electrons [2,3], all the more so if one is interested in truly dynamical situations. The extension to Time-Dependent DFT (TDDFT) has been formally established more recently [5,6,7] and it is still

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in development, concerning both formal and practical aspects [8]. Over the years, TDDFT has thus become one of the few, well founded theories, allowing to describe dynamical scenarios in complex systems. This is a key issue for understanding dynamical microscopic mechanisms, beyond mere energetic considerations, e.g. the process of electron emission as it is important in connection with laser irradiation.

A basic idea of (TD)DFT is to replace the involved correlated many-electron problem by an effective one-body description through the inclusion of exchange and correlation effects in a (as simple as possible) exchange and correlation functional, expressed in terms of the local density of the electrons. The simplest approximation to the exchange correlation functional is the Local Density Approximation (LDA), or Adiabatic Local Density Approximation (ALDA) in the time dependent case, which proved very useful in calculations of structure and low-amplitude excitations (optical response, direct one-photon processes) [4]. It can also be used as a first order approach in more violent dynamical processes involving huge energy deposits and/or large ionization as, for example, in the case of clusters or molecules subject to intense laser fields or to collision with highly charged particles [9].

However, LDA is plagued by a self-interaction error due to the fact that the direct Coulomb term and the exchange-correlation potential involve the total density including the particle on which the field actually acts. That Coulomb self-interaction is nicely canceled in a full Hartree-Fock treatment. However, the approximate treatment of exchange in LDA weakens this cancellation and a spurious self-interaction remains. As a consequence, LDA produces the wrong Coulomb asymptotic. The self-interaction thus spoils single-particle properties as, e.g., the Ionization Potential (IP) or the band gap in solids [10,11]. Another critical detail where LDA fails is the polarizability in chain molecules [12,13]. In dynamical situations, the self-interaction error will thus spoil the description of excitations involving ionization processes, especially in processes close to electron emission threshold. Correcting the self-interaction error requires a dedicated treatment known as the Self-Interaction Correction (SIC). Such a SIC complementing LDA static calculations was proposed in [14,15]. It has been used since then at various levels of refinement for structure calculations in atomic, molecular, cluster and solid state physics, see e.g. [16,17,18,19]. The original SIC scheme, however, leads to an orbital dependent mean field which causes several formal and technical difficulties. This aspect can be circumvented by treating SIC with optimized effective potentials (OEP), see [20] for a recent review. The resulting formalism is quite involved and usually treated with involving further approximations, as e.g. the Krieger-Li-Iafrate (KLI) approach [21,22]. These, however, can perturb some crucial physical features of SIC, particularly the trend to produce localized single-particle states [20].

The applications of SIC in time-dependent situations have, up to now, mostly been performed in the above mentioned approximate manners, e.g., the linearized treatment of [23], the use of averaged-density SIC [24], or the various versions of time dependent OEP-KLI [25,26,27]. The latter TDOEP-KLI, however, also suffers from inconsistencies. It leads, in particular, to the violation of zero force theorem and energy conservation [28]. There thus remains plenty of space for elaborating adequate versions of SIC, and even more so of TDSIC. The natural starting point, and benchmark for later approximations is a full TDSIC scheme. The aim of this paper is to present an exact thorough variational formulation of fully fledged TDSIC. We shall also propose a manageable propagation scheme which allows to obey all key conditions, namely the zero-force theorem, conservation of energy and conservation of orthonormality of the occupied single-particle orbitals. Our approach relies on a simple account of basic constraints and on the use of an important degree of freedom, namely the freedom of unitary transforms among occupied orbitals.

The paper is organized as follows. We first remind basic SIC equations in static case, introducing already the unitary transform degree of freedom. We then export the formalism in the time domain and discuss the properties of TDSIC. We finally show practical examples of applications in simple molecules and clusters, in particular in the case of irradiation processes.

2 Basic notations

Before attacking the question of the self-interaction correction, we want to introduce briefly generic notations and take the example of widely used Local Density Approximation (LDA) [29], [30] which serves as a basis for our further considerations. We shall work in the Kohn-Sham scheme of DFT [31]. The Kohn-Sham state is composed of a set single-particle wavefunctions $\{\psi_\alpha, \alpha = 1, \dots, N\}$ where N is the number of electrons of the system. These single-particle states have to be orthonormalized. This requirement will play a role later on. Both static and dynamical DFT schemes then amount to write effective one-body Schrödinger-like equations for the $\{\psi_\alpha, \alpha = 1, \dots, N\}$, called Kohn-Sham (KS) equations. In the KS scheme, the total electronic energy of the system E can be split into four terms :

$$E = E_{\text{kin}} + E_{\text{ext}} + E_{\text{H}} + E_{\text{xc}}. \quad (1)$$

The kinetic component E_{kin} is computed assuming non interacting ψ_α ; the direct Coulomb interaction E_{H} is computed classically (Hartree approximation [32]); the effect of the external potential (E_{ext} including in particular the ionic potential and possibly external fields such as that delivered by a laser) is computed exactly and finally the exchange Coulomb and the

electronic correlations are packed into the exchange correlation energy E_{xc} for which one has to construct approximations. All terms are functionals of the total electronic density $\rho(\mathbf{r})$.

The simplest and most widely used approximation for E_{xc} is the Local Density Approximation (LDA) in which one performs a local Fermi gas approximation for evaluating energies. The LDA serves as a starting point for many more involved approximations, in particular the SIC approximation we discuss in this paper. We thus assume that E_{xc} is computed in the LDA approximation. For the sake of simplicity in the notations, we shall pack together the (exact) Hartree and exchange correlation terms and note E_{LDA} the corresponding energy at LDA approximation : $E_{\text{LDA}} = E_{\text{H}} + E_{xc}$. One can then derive the KS equations (stationary or time dependent) by standard variational techniques which leads to single electron KS equations with LDA single electron Hamiltonian

$$\hat{h}_{\text{LDA}} = -\frac{\hbar^2 \Delta}{2m} + U_{\text{ext}} + U_{\text{LDA}}[\rho] \quad , \quad (2)$$

$$U_{\text{LDA}}[\varrho] = \left. \frac{\delta E_{\text{LDA}}}{\delta \rho} \right|_{\rho=\varrho} = U_{\text{H}}[\varrho] + U_{xc}[\varrho] \quad . \quad (3)$$

As outlined in the introduction, the LDA approximation suffers from the self-interaction error. For example, its direct Coulomb part $U_{\text{H}}[\rho]$ is a functional of the total density which is computed by summing over all occupied single electron densities ($\rho = \sum_{\alpha} \rho_{\alpha}$). Then a particle α will feel its own Coulomb repulsion and this spurious self-interaction is not properly removed by the exchange term in LDA. This thus calls for a SIC treatment.

3 Stationary SIC

3.1 SIC functional and Hamiltonian

The starting point is the SIC energy functional (following notations of section 2)

$$E_{\text{SIC}} = E_{\text{kin}} + E_{\text{ext}} + E_{\text{ion}} + E_{\text{LDA}}[\rho] - \sum_{\beta=1}^N E_{\text{LDA}}[|\psi_{\beta}|^2] \quad (4)$$

where the total density is $\rho = \sum_{\alpha} \rho_{\alpha}$ with $\rho_{\alpha} = |\psi_{\alpha}|^2$. Note that all summations run over occupied states only. The corresponding one-body Hamiltonian is obtained from variation of E_{SIC} with respect to ψ_{α}^* as

$$\frac{\delta E_{\text{SIC}}}{\delta \psi_{\alpha}^*} = \hat{h}_{\alpha} \psi_{\alpha} , \quad (5a)$$

$$\hat{h}_{\alpha} = \hat{h}_{\text{LDA}} - U_{\alpha} , \quad (5b)$$

$$U_{\alpha} = U_{\text{LDA}}[|\psi_{\alpha}|^2] . \quad (5c)$$

The emerging one-body Hamiltonian \hat{h}_{α} depends on the state ψ_{α} on which it acts through the SIC term U_{α} . Thus it is not invariant under unitary transformations within the sub-space of occupied orbitals.

3.2 The stationary SIC equations

3.2.1 Variational derivation

The static SIC equations are derived by minimization of the SIC energy (4) together with the condition that the single-particle orbitals are orthonormalized. This amounts to the variational equation

$$0 = \delta_{\psi_{\alpha}^*} \left[E_{\text{SIC}} - \sum_{\alpha, \beta} (\psi_{\alpha} | \psi_{\beta}) \lambda_{\beta\alpha} \right] \quad (6)$$

where $\lambda_{\alpha\beta}$ is a matrix of Lagrangian multipliers, which is non-diagonal in general. As worked out in appendix A, $\lambda_{\alpha\beta}$ is a hermitian matrix. Evaluation of the variation yields the stationary equations

$$\hat{h}_{\alpha} |\psi_{\alpha}\rangle = \sum_{\beta} |\psi_{\beta}\rangle \lambda_{\beta\alpha} , \quad (7a)$$

$$\lambda_{\beta\alpha} = (\psi_{\beta} | \hat{h}_{\alpha} | \psi_{\alpha}) . \quad (7b)$$

We consider the hermitian conjugate equation

$$(\psi_{\beta} | \hat{h}_{\beta} = \sum_{\alpha} \lambda_{\alpha\beta}^* (\psi_{\alpha} | = \sum_{\alpha} \lambda_{\beta\alpha} (\psi_{\alpha} |$$

(where we have exploited hermiticity of $\lambda_{\beta\alpha}$), project Eq. (7a) with $(\psi_{\beta} |$, its conjugate with $|\psi_{\alpha}\rangle$, and take the difference of these two equations. This yields $0 = (\psi_{\beta} | \hat{h}_{\beta} - \hat{h}_{\alpha} | \psi_{\alpha})$. The only state-dependence in \hat{h}_{α} stems from U_{α} . Thus we remain with the condition

$$0 = (\psi_{\beta} | U_{\beta} - U_{\alpha} | \psi_{\alpha}) . \quad (8)$$

We call it the symmetry condition. It plays a crucial role in all SIC considerations. It was first introduced in a particular case by Pederson *et al.* [16] and

since then addressed by several authors [17,19,29]. The above derivation indicates clearly the relation between symmetry condition Eq. (8) and orthonormality constraint. We shall discuss this condition further at several places. Note that it is trivially fulfilled in case of state-independent Hamiltonians for which $\hat{h}_\alpha = \hat{h}_\beta = \hat{h}$, as it is the case in LDA or Hartree-Fock.

A word is in order about the SIC Hamiltonian \hat{h}_α . It depends on the state on which it acts. Thus one has to be extremely careful with everything one knows from Quantum Mechanics and Hilbert space. The \hat{h}_α is not a linear operator which is obvious from the fact that the operation $\hat{h}_\alpha [|\psi_\alpha\rangle c_\alpha + |\psi_\beta\rangle c_\beta]$ is not defined at all. We will also see more clearly in the next section that the SIC Hamiltonian is not hermitian.

3.2.2 State-independent notation

For formal manipulations, it may be simpler to recast the state dependent SIC Hamiltonian \hat{h}_α into a compact form as

$$\hat{h}_{\text{SIC}} = \hat{h}_{\text{LDA}} - \sum_{\alpha} U_{\alpha} |\psi_{\alpha}\rangle \langle \psi_{\alpha}| \quad . \quad (9)$$

The part sensitive to single-particle states has been expressed in terms of projectors $|\psi_{\alpha}\rangle \langle \psi_{\alpha}|$ such that the SIC Hamiltonian (9) is not explicitly state-dependent, but $\hat{h}_{\text{SIC}} |\psi_{\alpha}\rangle$ remains equivalent to $\hat{h}_{\alpha} |\psi_{\alpha}\rangle$. The form (9) is advantageous for formal considerations. The SIC equations become now equivalently

$$\hat{h}_{\text{SIC}} |\psi_{\alpha}\rangle = \sum_{\beta} |\psi_{\beta}\rangle \lambda_{\beta\alpha} \quad , \quad (10a)$$

$$\lambda_{\beta\alpha} = \langle \psi_{\beta} | \hat{h}_{\text{SIC}} | \psi_{\alpha} \rangle \quad . \quad (10b)$$

The symmetry condition is derived as above. We build the hermitian conjugate equation, take the difference of the two equations, and exploit the fact that the Lagrangian matrix is hermitian. This yields

$$0 = \langle \psi_{\beta} | \hat{h}_{\text{SIC}}^{\dagger} - \hat{h}_{\text{SIC}} | \psi_{\alpha} \rangle \quad (10c)$$

which is equivalent to the symmetry condition in the form (8) when dropping the state independent part \hat{h}_{LDA} and evaluating the projectors.

It is interesting to note that the form (9) shows clearly the possible non-hermiticity of the SIC Hamiltonian. This makes the symmetry condition (10c), or equivalently (8), a non-trivial and crucial part of the SIC equations. Superficially, it makes the impression of a condition ensuring hermiticity of the

SIC Hamiltonian \hat{h}_{SIC} . But one has to keep in mind that condition (10c) is restricted to the space of occupied orbitals. Thus the symmetry condition forces restoration of hermiticity only in the sub-space of occupied states.

3.2.3 Projector notation

The SIC equation can be recast in a particularly compact form when introducing the projection operator onto the unoccupied space

$$\hat{\Pi}_{\perp} = \hat{1} - \sum_{\beta} |\psi_{\beta}\rangle\langle\psi_{\beta}|. \quad (11)$$

This allows to reformulate the SIC equations (7a) or (10a) as

$$\hat{\Pi}_{\perp} \hat{h}_{\alpha} |\psi_{\alpha}\rangle = 0 \quad \text{or} \quad \hat{\Pi}_{\perp} \hat{h}_{\text{SIC}} |\psi_{\alpha}\rangle = 0 \quad (12)$$

showing that these equations serve to establish a decoupling of occupied and unoccupied space which is a general feature of any mean-field equation. The new key feature of the SIC equations is the additional symmetry condition, Eqs. (8) or (10c), which comes into play because the SIC energy (4) is not unitary invariant such that there is a unique optimum for the occupied states.

3.2.4 Single-particle energies

The symmetry condition minimizes the SIC energy and does that by producing more or less localized states which maximize the Coulomb SIC of each state (see the later discussion). This produces in general non-diagonal Lagrangian matrices $\lambda_{\alpha\beta}$ from which single-particle energies cannot immediately be read off. However, the necessary information is contained in that matrix. The single-particle energies can be defined as the eigenvalues ε_i of $\lambda_{\alpha\beta}$ obtained from the secular equation in occupied space

$$\sum_{\beta} \lambda_{\alpha\beta} v_{\beta i} = \varepsilon_i v_{\alpha i} \quad (13)$$

where $v_{\alpha i}$ are coefficients of the appropriate unitary transformation.

3.3 Double-set formulation of SIC

Thus far, the formulation of SIC for stationary states is complete and manageable. The computation of single-particle energies motivates an alternative formulation which deals with two different, but related, sets of occupied single-particle states. We will thus discuss in this section a double-set formulation

of stationary SIC. It is an interesting, but not compulsory, alternative for the static case. But a double-set technique becomes almost inevitable for TDSIC. The present (static) section serves, so to say, as a preparation.

3.3.1 Two sets of occupied states

The computation of single-particle energies, as outlined in section 3.2.4, leads naturally to a second set of single-particle states $\{\varphi_i\}$ connected to the original set by a unitary transformation within occupied space

$$\varphi_i = \sum_{\alpha=1}^N \psi_{\alpha} v_{\alpha i} \quad , \quad \sum_{\alpha} v_{\alpha i}^* v_{\alpha j} = \delta_{ij} \quad . \quad (14)$$

The set $\{\varphi_i\}$ is associated to the single-particle energies ε_i and so diagonal in energy space. We call it diagonalizing set. The set $\{\psi_{\alpha}\}$ optimizes the SIC potentials and does that by some localization. We call it the localizing set. The diagonalizing set is compact in energy space at the price of larger spatial spreading and the localizing set minimizes spatial extension while enhancing energy variance. Both sets have their value. A proper combination of them will become particularly important in the dynamical case, see section 4.

3.3.2 Double-set SIC equations

The first SIC equation (10a) becomes particularly simple in terms of the diagonalizing set. It reads now

$$\hat{h}_{\text{SIC}}|\varphi_i\rangle = \varepsilon_i|\varphi_i\rangle \quad . \quad (15a)$$

That equations provides the decoupling from unoccupied space as shown in section 3.2.3. The symmetry condition cares for determining the localizing set within occupied space which now shrinks to a condition for the transformation coefficients $v_{\alpha i}$. We emphasize that by rewriting

$$v_{i\alpha} \quad \longleftrightarrow \quad 0 = (\psi_{\beta}|U_{\beta} - U_{\alpha}|\psi_{\alpha}) \quad . \quad (15b)$$

That localizing set is needed to compute the SIC potentials U_{α} and with it, \hat{h}_{SIC} .

The double-set equations (15) can be used for an alternative solution scheme. However, there is no gain in efficiency as compared to the previous scheme, i.e. solving first the SIC equations (7) with a single set $\{\psi_{\alpha}\}$ and afterwards diagonalizing the Lagrangian matrix $\lambda_{\beta\alpha}$ to obtain the single-particle energies.

3.3.3 Variational derivation

It is instructive to derive double-set SIC directly from the stationary variational principle. To that end, we consider the diagonalizing set $\{\varphi_i\}$ and the transformation coefficients $v_{\alpha i}$ as variational degrees of freedom. The SIC functional is to be minimized with boundary conditions of orthonormality of the φ_i and $v_{\alpha i}$. This means to minimize the functional

$$F[\varphi_i, v_{\alpha i}] = E_{\text{SIC}}[\varphi_i, v_{\alpha i}] - \sum_{k,j} (\varphi_k | \varphi_j) \theta_{jk} - \sum_{\alpha\beta} \left(\sum_i v_{\alpha i}^* v_{\beta i} \right) \Lambda_{\beta\alpha} . \quad (16)$$

It is interesting to compare the extension with LDA. In that case, one deals with an energy functional which is invariant under unitary transformations amongst occupied states. That allowed to perform always a unitary transformation such that $\sum_{k,j} (\varphi_k | \varphi_j) \theta_{jk} \longrightarrow \sum_j (\varphi_j | \varphi_j) \varepsilon_j$ from which one obtains immediately the energy-diagonal LDA equations by variation. The SIC functional (4) is not unitary invariant which, in turn, led to the notoriously non-diagonal Lagrangian matrix. The functional (16) formulated in terms of the double-set can now be considered again as being unitary invariant with respect to the φ_i because any rotation within the $\{\varphi_i\}$ can be compensated by proper counter-rotation of the $v_{i\alpha}$. Thus we can always perform a transformation to the simpler functional

$$F[\varphi_i, v_{\alpha i}] = E_{\text{SIC}}[\varphi_i, v_{\alpha i}] - \sum_j (\varphi_j | \varphi_j) \varepsilon_j - \sum_{\alpha\beta} \left(\sum_i v_{\alpha i}^* v_{\beta i} \right) \Lambda_{\beta\alpha} .$$

First, we perform variation with respect to the φ_i^* . The key piece is

$$\begin{aligned} \frac{\delta E_{\text{SIC}}}{\delta \varphi_i^*(\mathbf{r})} &= \sum_{\alpha} \frac{\delta \psi_{\alpha}^*(\mathbf{r})}{\delta \varphi_i^*(\mathbf{r})} \frac{\delta E_{\text{SIC}}}{\delta \psi_{\alpha}^*(\mathbf{r})} = \sum_{\alpha} (\mathbf{r} | \hat{h}_{\alpha} | \psi_{\alpha}) v_{\alpha i}^* = \sum_{\alpha} (\mathbf{r} | \hat{h}_{\alpha} | \psi_{\alpha}) (\psi_{\alpha} | \varphi_i) \\ &= (\mathbf{r} | \hat{h}_{\text{SIC}} | \varphi_i) . \end{aligned}$$

Thus we obtain from $\delta_{\varphi_i^*} F = 0$ the first SIC equation (15a). In a second step, we perform variation with respect to the transformation coefficients $v_{\alpha i}$. We exploit

$$\frac{\delta E_{\text{SIC}}}{\delta v_{\alpha i}} = \int d^3\mathbf{r} \frac{\delta \psi_{\alpha}^*}{\delta v_{\alpha i}} \frac{\delta E_{\text{SIC}}}{\delta \psi_{\alpha}^*} = (\varphi_i | \hat{h}_{\text{SIC}} | \psi_{\alpha}) = (\varphi_i | \hat{h}_{\alpha} | \psi_{\alpha})$$

and obtain from variation $\sum_{\beta} v_{\beta i}^* (\psi_{\beta} | \hat{h}_{\alpha} | \psi_{\alpha}) = \sum_{\beta} \sum_i v_{\beta i}^* \Lambda_{\beta\alpha}$ and subsequently $(\psi_{\beta} | \hat{h}_{\alpha} | \psi_{\alpha}) = \Lambda_{\beta\alpha}$. Similar as in sections 3.2.1 and 3.2.2, we build the hermitian conjugate and take the difference. This yields then the symmetry condition (15b).

Thus the direct variational derivation recovered nicely the double-set formulation of stationary SIC. It is important to remark that the symmetry condition (15b) results from minimization of the SIC energy with orthonormality constraint for fixed φ_i .

3.3.4 The existence of a solution to the symmetry condition

The symmetry condition Eq. (15b) is as such a highly non-linear equation. One may wonder whether a solution exists in general. We have seen in the above section that the symmetry condition simply emerges from minimizing the total energy in the reduced space of occupied single-particle orbitals. There necessarily exists an energy minimum in the restricted space and thus that there always exists a solution to the symmetry condition. This is a crucial feature because the symmetry condition is always present in any formulation of SIC, static and time-dependent.

4 Time Dependent SIC (TDSIC)

Now that a proper SIC formulation has been given in the static case, we can consider the dynamical case along the same line. The diagonal formulation will become crucial.

4.1 Derivation of TDSIC

The TDSIC equations are obtained from the principle of stationary action using the SIC energy functional (4)

$$0 = \delta S \quad , \quad S = \int_{t_0}^t dt' \left(E_{\text{SIC}} - \sum_{\alpha} (\psi_{\alpha} | i\hbar \partial_t | \psi_{\alpha}) - \sum_{\beta, \gamma} (\psi_{\beta} | \psi_{\gamma}) \lambda_{\gamma\beta} \right) , \quad (17)$$

explicitly including the orthonormality constraint with Lagrange multipliers $\lambda_{\gamma\beta}$ as in the static case. Note that the matrix of Lagrangian multipliers is hermitian as shown in appendix A. Variation with respect to ψ_{α}^* yields the TDSIC equation for the propagation of single-particle orbitals as

$$\left(\hat{h}_{\text{SIC}} - i\hbar \partial_t \right) | \psi_{\alpha} \rangle = \sum_{\beta} | \psi_{\beta} \rangle \lambda_{\beta\alpha} \quad , \quad (18a)$$

$$\lambda_{\beta\alpha} = (\psi_{\beta} | \hat{h}_{\alpha} - i\hbar \partial_t | \psi_{\alpha}) \quad . \quad (18b)$$

The relation (18b) for the Lagrangian multipliers becomes non-trivial by the fact that it is hermitian, i.e.

$$\lambda_{\beta\alpha} = \lambda_{\alpha\beta}^* . \quad (18c)$$

This can be exploited by the same steps as performed in the static sections 3.2.1 and 3.2.2. We build the hermitian conjugate of Eq. (18b), insert Eq.

(18c), and take the difference. This yields once again the symmetry condition

$$0 = (\psi_\beta | U_\beta - U_\alpha | \psi_\alpha) , \quad (18d)$$

now for TDSIC and to be fulfilled at each instant of time.

4.2 Solution of TDSIC with a double-set of orbitals

The TDSIC equations (18) are very involved and it is extremely hard to deduce a transparent numerical stepping scheme from them. Time evolution is related to energies and we have seen in static SIC that single-particle energies and SIC potentials are taking different cuts through the single-particle Hilbert space. The concept of single-particle energies led us naturally to a double-set strategy, see section 3.3.2. That strategy becomes extremely helpful in developing a solution scheme for TDSIC.

We disentangle the involved equations of motion (18) by distinguishing the SIC localizing set $\{\psi_\alpha(t)\}$ from a propagating set $\{\varphi_i(t)\}$. The both are connected by a unitary transformation amongst occupied states

$$|\varphi_i(t)\rangle = \sum_{\beta=1}^N |\psi_\beta(t)\rangle v_{\beta i}(t) \quad , \quad \sum_{\alpha} v_{\alpha i}^*(t) v_{\alpha j}(t) = \delta_{ij} . \quad (19)$$

That is the time-dependent generalization of the transformation (14). The transformation coefficients depend also on time and the transformation is performed at each instant of time.

We now choose the propagating set φ_i such that it diagonalizes the Lagrangian matrix $\lambda_{\alpha\beta}$. Thus we obtain $(\hat{h}_{\text{SIC}} - i\hbar\partial_t) |\varphi_i\rangle = \lambda_{ii} |\varphi_i\rangle$. The λ_{ii} yields an irrelevant phase and can be ignored. There remains

$$(\hat{h}_{\text{SIC}} - i\hbar\partial_t) |\varphi_i\rangle = 0 , \quad (20)$$

The $\{\varphi_i\}$ can then be propagated in standard manner as:

$$|\varphi_i(t)\rangle = \exp \left\{ -\frac{i}{\hbar} \int_{t_0}^t dt' \hat{h}_{\text{SIC}}(t') \right\} |\varphi_i(t_0)\rangle . \quad (21a)$$

This procedure implies that the symmetry condition (18d) is fulfilled at each instant of time. To that end, we exploit the freedom of choice of $v_{\alpha i}$. Similar as in static SIC, we know that we can always determine the $v_{\alpha i}$ such that

$$v_{\alpha i}(t) \quad \longleftrightarrow \quad 0 = (\psi_\beta | U_\beta - U_\alpha | \psi_\alpha) . \quad (21b)$$

The interlaced stepping of Eqs. (21) provides a manageable solution scheme. Further formal properties will be discussed in sections 4.4 and 4.5. The prac-

tical applicability and stability of the scheme is proven by the many results presented in section 5.

Note that the above propagator in Eq. (21a) is not strictly unitary because \hat{h}_{SIC} is not hermitian. But the hermiticity within occupied space, Eq. (18c), guarantees that the propagation (21a) preserves orthonormality within occupied space, i.e. $(\varphi_i(t)|\varphi_j(t)) = \delta_{ij}$. That suffices for our purposes.

4.3 Projector notation

An instructive alternative formulation can be given using the operator of projection onto the unoccupied space, the $\hat{\Pi}_{\perp}$ as defined in eq. (11). This allows to recast the TDSIC equation into the particularly compact form

$$\hat{\Pi}_{\perp}(\mathrm{i}\hbar\partial_t - \hat{h}_{\text{SIC}})|\psi_{\alpha}) = 0 \quad .$$

It defines the part of the change of the wavefunctions evolving into the space orthogonal to the already occupied states. The evolution inside the occupied states is again prescribed by the symmetry condition (21b).

4.4 Direct variational formulation of double-set TDSIC

In section 4.1, we deduced TDSIC from variation of the action (17) with respect to the single-particle states $\{\psi_{\alpha}\}$, in a one-set strategy, while imposing their orthonormality. The double-set TDSIC was introduced in section 4.2 as a means to solve the TDSIC equations. In this section, we are going to derive double-set TDSIC directly from the time-dependent variational principle. This makes the derivation of TDSIC especially straightforward and it will add new aspects to the scheme.

Starting point is again the action (17), but now formulated in terms of the two sets of orbitals, the SIC orbitals $\{\psi_{\alpha}\}$ and the propagating orbitals $\{\varphi_i\}$, related by a unitary transformation (19). Variation with imposing orthonormality of the $\{\varphi_i\}$ and $\{v_{i\alpha}\}$ reads

$$\begin{aligned} S[\varphi_i, v_{i\alpha}] = \int_{t_0}^t dt' \Big(& E_{\text{SIC}}[\psi_{\alpha}] - \sum_{\alpha} (\varphi_i | \mathrm{i}\hbar\partial_t | \varphi_i) - \sum_{k,l} (\varphi_k | \varphi_j) \theta_{jk} \\ & - \sum_{\alpha\beta} \left(\sum_i v_{\alpha i}^* v_{\beta i} \right) \Lambda_{\beta\alpha} \Big) \quad . \end{aligned} \quad (22)$$

As proven in appendix A, the Lagrangian matrices θ_{jk} and $\Lambda_{\beta\alpha}$ are hermitian. Note that the transformation (19) leaves the time-derivative term invariant

and we have chosen to express it in terms of the propagating set which is here the natural choice. The SIC energy (4) is not unitary invariant and needs to be expressed in terms of the SIC set $\{\psi_\alpha\}$. We ought to remind, however, that the $\{\psi_\alpha\}$ are given through the $\{\varphi_i\}$ via Eq. (19) such that we consider the action as a functional of the $\{\varphi_i\}$ and $\{v_{\alpha i}\}$.

First, we perform variation with respect to the coefficients of the unitary transformation. We note that, among the first three terms, only E_{SIC} depends on them and thus $\delta_{v_{\alpha i}} S = 0$ leads to

$$\delta_{v_{\alpha i}} \left(E_{\text{SIC}} - \sum_{\alpha\beta} \sum_i v_{i\alpha}^* v_{i\beta} \Lambda_{\beta\alpha} \right) = 0$$

and subsequently to

$$\int d^3\mathbf{r} \left(\underbrace{\frac{\partial \psi_\alpha^*}{\partial v_{\alpha i}}}_{\varphi_i^*} \underbrace{\frac{\partial E}{\partial \psi_\alpha^*}}_{\hat{h}_{\text{SIC}}\psi_\alpha} - \sum_\beta v_{\beta i}^* \Lambda_{\beta\alpha} \right) = 0 \quad ,$$

where \hat{h}_{SIC} is given in Eq. (9). That can be rewritten in the more familiar form as $(\varphi_i | \hat{h}_\alpha | \psi_\alpha) = \sum_\beta v_{\beta i}^* \Lambda_{\beta\alpha}$ and finally be transformed to

$$(\psi_\beta | \hat{h}_\alpha | \psi_\alpha) = \Lambda_{\beta\alpha} \quad .$$

Considering the complex conjugate of that equation and exploiting hermiticity of $\Lambda_{\beta\alpha}$, we find $(\psi_\beta | \hat{h}_\beta - \hat{h}_\alpha | \psi_\alpha) = 0$ and from this the crucial symmetry condition

$$v_{\alpha i} \longleftrightarrow (\psi_\beta | U_\beta - U_\alpha | \psi_\alpha) = 0 \quad , \quad (23a)$$

which is here to be understood as a condition determining the coefficients $v_{i\alpha}$ for given set $\{\varphi_i\}$.

In a second step, we perform variation with respect to the propagating orbitals. Evaluating the variational equation $\delta_{\varphi_i^*} S = 0$ yields

$$(\hat{h}_{\text{SIC}} - i\hbar\partial_t)|\varphi_i) = \sum_j |\varphi_j)\theta_{ji} \quad , \quad \theta_{ji} = (\varphi_j | \hat{h}_{\text{SIC}} - i\hbar\partial_t | \varphi_i)$$

The Lagrangian matrix is again hermitian, i.e. $\theta_{ij} = \theta_{ji}^*$ which, in turn, implies the "weak" hermiticity condition that \hat{h}_{SIC} is hermitian in the sub-space of occupied states. Thus this Hamiltonian can be diagonalized and it is sufficient to solve $(\hat{h}_{\text{SIC}} - i\hbar\partial_t)|\varphi_i) = \eta_i|\varphi_i)$. The Floquet index η_i produces a global phase factor which is irrelevant for our purposes and can be dropped. Thus we remain with the time-dependent mean-field equation for the propagating states

$$(\hat{h}_{\text{SIC}} - i\hbar\partial_t)|\varphi_i) = 0 \quad . \quad (23b)$$

The propagation (23b) together with the symmetry condition (23a) constitute the complete set of dynamical equations for TDSIC with double set. It is satisfying to see that both equations can be derived out of one variational principle. The difference to TDSIC with one set as derived in section 4.1 is that we now allow for two independent sets of orbitals connected by a unitary transformation. The variational scheme exploits that additional freedom to deliver correctly double-set TDSIC as the optimal scheme when dealing with two sets.

We see also that the symmetry condition emerges from variation of E_{SIC} much similar as in the static case. The reasoning of section 3.3.4 proving the existence of a solution for the symmetry condition does also apply here.

4.5 Conservation laws

The TDSIC equations yield energy conservation as long as the external field remain independent on time. And they also fulfill the zero-force theorem [28,33,34]. The reasoning is simple. The LDA functional and its SIC extension are invariant under time- and space-translations. The same holds for the orthonormality constraints. The equations of motion are derived variationally without further restrictions and approximations. This yields energy conservation from time translational invariance. The space-translational invariance would yield momentum-conservation if the electrons were alone. That feature is broken by external fields. But what remains is the fact that the electrons cannot exert a force on themselves which is the content of the zero-force theorem. More explicit proofs are given in appendix D.

4.6 Static limit

It is also interesting to consider the stationary limit of TDSIC. To that end, we use TDSIC in double-set set formulation. We identify

$$\varphi_i(\mathbf{r}, t) = \varphi_i(\mathbf{r}, \mathbf{0})e^{-i\epsilon_i t/\hbar}.$$

Inserting that into the TDSIC equation (20), one immediately recovers the static SIC equation (15a) for the diagonalizing states. The single-particle wavefunctions change in time only by a phase factor. The sub-space of occupied states thus remains constant in time and the symmetry condition always minimizes the same sub-space. And that yields the time-independent localized states ψ_α of the static problem.

5 Test cases and numerical realization

5.1 Models

We want to test the above discussed TDSIC formalism in truly dynamical situations. The ultimate goal of these studies is to describe dynamically the irradiation of various molecules, in particular organic ones. A correct modeling of the IP is then crucial and TDSIC becomes compulsory, especially close to emission threshold. We have developed since long fully fledged coupled electronic dynamics for clusters [35] and used extensively at TDLDA level and in simplified SIC schemes [24]. We thus have at hand a powerful tool for analyzing irradiation dynamics. Still, the proposed TDSIC formalism is quite involved. In order to have a more flexible testing tool, we have thus developed a one-dimensional (1D) model mocking up typical atoms and simple (linear !) molecules. This will serve as a starter to study the properties of TDSIC. And we will finally complement these schematic results by realistic ones with the full 3D approach.

5.1.1 The simplified 1D model

To test numerically the SIC scheme, we take up the test case of [36] consisting in a one-dimensional model for a molecule. Spin is not taken into account explicitly and all electrons are assumed to have the same spin such that they all explore the full exchange effects. Apart from its simplicity and computational cost, the 1D test case has also the advantage to be a much more sensitive test of orthonormalization than in 3D calculations.

For the electron-electron interaction, we use a smoothed Coulomb potential (in Hartree units)

$$v(x, x') = \frac{1}{\sqrt{(x - x')^2 + a}} \quad . \quad (24)$$

Starting with this "elementary" interaction, we construct the corresponding LDA energy functional for exchange only. Working at the level of exchange only allows to have fully fledged time-dependent HF (TDHF) calculations as a benchmark to which TDSIC calculations can be compared. The detailed calculation of the LDA energy is presented in appendix C. The resulting LDA exchange potential (γ is the possible degeneracy number, equal to 1 in the next results) reads:

$$U_{\text{LDA}}^x[\rho] = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} dy \frac{\sin(\frac{2\pi\rho(x)}{\gamma}y)}{y\sqrt{y^2 + a}} \quad . \quad (25)$$

For the electron-ion interaction, we also use a smoothed Coulomb potential (in Hartree units) of the form

$$U_{\text{ion}}(x) = -\frac{Nz}{\sqrt{(x - R/2)^2 + b}} - \frac{N(1 - z)}{\sqrt{(x + R/2)^2 + b}} \quad , \quad (26)$$

where R is the inter-ionic distance which allows the possibility to compute bi-atomic molecules, N is the number of electrons and $z \in [0, 1]$ is an asymmetry parameter. If $z = 0.5$ and $R=0$, we recover the atomic case. If $z=0.5$ and $R \neq 0$, we obtain the bi-atomic symmetric molecular case. If $z \neq 0.5$ and $R \neq 0$, we get the asymmetric molecular case, which provides a more critical probe of the role of orthonormalization.

The a and b parameter for a two-electron system are scaled to approach the experimental H_2 bond length ($1.4 a_0$) and ionization potential (0.57 Ha). With $a=0.8$ and $b=0.5$, we obtain a H_2 bond length of $1.6 a_0$ and an ionization potential of 0.5 Ha. Depending on the case, we use slightly varied values which will be indicated.

5.1.2 Full 3D model

The 3D calculations follow the standard techniques as we use it since long [9,35]. The electron wavefunctions and spatial fields are represented on a Cartesian grid in three-dimensional coordinate space. The spatial derivatives are evaluated via fast Fourier transformation. The ground state configurations were found by adapting the accelerated gradient iteration for the electronic wavefunctions [37] to SIC. Propagation is done by the time-splitting method for the electronic wavefunctions [38] augmented by updates of the symmetry condition as explained below. For the energy functional, we employ the widely used functional of [39].

5.2 Solution scheme for stationary SIC

In straightforward generalization of the damped gradient step [37], we solve the static Eqs. (7) iteratively as

$$\psi_{\alpha}^{(\text{new})} = \mathcal{O} \left\{ \psi_{\alpha} - \frac{\delta_{\text{step}}}{\hat{T} + E_{\text{damp}}} \left[\hat{h}_{\alpha} \psi_{\alpha} - \sum_{\beta} \psi_{\beta} \lambda_{\beta\alpha} \right] \right\} \quad , \quad (27a)$$

$$\lambda_{\beta\alpha} = \frac{(\psi_{\beta} | \hat{h}_{\alpha} | \psi_{\alpha}) + (\psi_{\alpha} | \hat{h}_{\beta} | \psi_{\beta})^*}{2} \quad , \quad (27b)$$

where \mathcal{O} stands for orthonormalization. The step (27a) provides simultaneously a complete solution including a matching of the symmetry condition, because the latter is implicitly taken into account in the symmetrization of the $\hat{\lambda}$ matrix.

It turns out that the step (27a) converges, however very slowly, and that the symmetry condition causes the delay. We speed up the iterations improving the symmetry condition explicitly in each step. This is done by a unitary transformation within occupied states. The coefficients of that unitary transformation are also determined by a gradient iteration as

$$u_{i\gamma}^{(\text{new})} = \mathcal{O} \left\{ u_{i\gamma}^{(\text{old})} - \eta D_{i\gamma} \right\} \quad , \quad (28a)$$

$$D_{i\gamma} = \partial_{u_{i\gamma}^*} \left[E_{\text{SIC}} - \sum_{j,\alpha,\beta} u_{j\alpha}^* u_{j\beta} \lambda_{\beta\alpha} \right] = -(\varphi_i | U_\gamma | \psi_\gamma) - \sum_{\beta} u_{i\beta} \lambda_{\beta\gamma} \quad , \quad (28b)$$

where the “driving force” $D_{i\gamma}$ is obtained by variation of the SIC energy with respect to $u_{i\gamma}^*$. That interlaced combination of damped gradient step and symmetry condition converges acceptably fast.

Depending on the initial conditions, it may take a while until the interlaced iteration has found its path to the properly localized wavefunctions. A further substantial acceleration can be achieved by performing in the initial phase once in a while a localization transformation. There are several localization criteria at choice [40,41]. We found very efficient improvements with simply minimizing the sum of the spatial variances of the single-electron states, defined as

$$\Delta\psi = \sum_{\alpha} \left[(\psi_{\alpha} | \mathbf{r}^2 | \psi_{\alpha}) - (\psi_{\alpha} | \mathbf{r} | \psi_{\alpha})^2 \right] . \quad (29)$$

5.3 Propagating TDSIC numerically

In the time-dependent case, the only manageable way to propagate TDSIC is to use the double-set strategy. For one time step δt , the propagation proceeds as follows. We first evaluate $\varphi_i \left(t + \frac{\delta t}{2} \right) = \exp \left[-\frac{i\delta t}{2\hbar} \hat{h}_{\text{SIC}}(t) \right] \varphi_i(t)$, where $\hat{h}_{\text{SIC}}(t)$ is obtained by the chain :

$$\varphi_i(t) \xrightarrow{\text{Eqs. (18d,19)}} \{v_{i\beta}(t), \psi_{\alpha}(t)\} \xrightarrow{\text{Eq. (9)}} \hat{h}_{\text{SIC}}(t). \quad (30)$$

Gradient iteration, similar to Eq. (28b), is used to solve Eq. (18d) for the $v_{i\beta}(t)$, from which one deduces the $\psi_{\alpha}(t)$ and $\hat{h}_{\text{SIC}}(t)$. The $\varphi_i(t + \delta t/2)$ thus obtained are used to compose $\hat{h}_{\text{SIC}}(t + \delta t/2)$ similarly using the chain (30). We

finally compute

$$\varphi_i(t + \delta t) = \exp \left[-\frac{i\delta t}{\hbar} \hat{h}_{\text{SIC}} \left(t + \frac{\delta t}{2} \right) \right] \varphi_i(t). \quad (31)$$

After all, the scheme as explained here works reliably and robust in 1D as well as in 3D. We checked conservation of energy and orthonormality and found it fully satisfying in all cases. The symmetry condition is, of course, fulfilled all along the time evolution by construction.

A proper computation of ionization requires to prevent reflection of electrons which have been ejected from the molecule and are now impinging on the bounds of the numerical grid. We do that by employing boundary conditions. To that end, an absorbing zone of a few grid points is defined. For each time step, the part of electronic wavefunctions which has penetrated into that zone is eliminated by a mask function, for details see [9,35].

6 Results and discussion

6.1 Stationary state

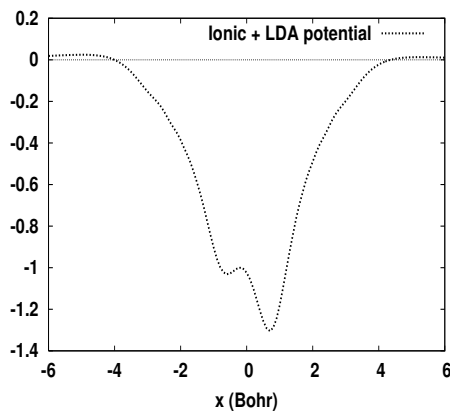


Fig. 1. The mean-field potential from ionic background and LDA-part (without SIC-parts) obtained in the 1D model with 2 electrons. The model parameters are $a = 0.8 a_0$, $b = 0.5 a_0$, $R = 1.5 a_0$, and $z = 0.4$.

It is well known that static SIC has a tendency to localize spatially the orbitals [16]. We analyze this fact on the example of the stationary solution for a system of two electrons in the 1D model developed in section 5.1.1. Note that $z \neq 0.5$, i.e. we enforce a slight asymmetry. The resulting ionic + LDA potential obtained for a SIC solution is plotted in Fig. 1. Note that the SIC potential

cannot be plotted easily because of its state-dependence. The resulting single-particle energies ϵ_i are $-0.88 / -0.32$ for LDA, $-1.18 / -0.60$ for SIC, and $-1.24 / -0.55$ for the HF benchmark. Note that the results of SIC comes close to HF as it should be.

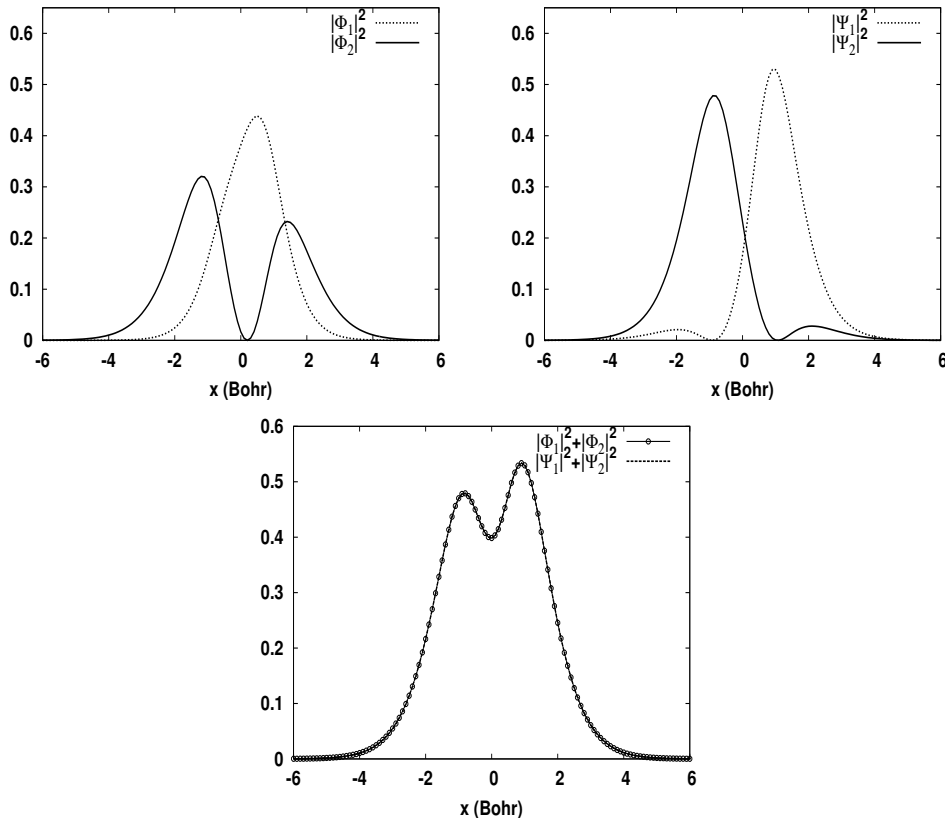


Fig. 2. Static SIC densities obtained in the 1D model with 2 electrons. Top left: Densities from diagonal wavefunctions, $|\varphi_i|^2$. Top right: Densities from localized wavefunctions, $|\psi_\alpha|^2$, obtained after unitary transformation. Bottom: Comparison of the total density calculated from both sets of wavefunctions.

Fig. 2 compares the single-particle densities of the localized wavefunctions $|\psi_\alpha|^2$ with those of the energy-diagonal wavefunctions $|\varphi_i|^2$. It is obvious that the localized densities are much better concentrated in space than the diagonal ones. The total density (lower panel), of course, remains the same for both cases because the two sets are linked by a unitary transformation.

We are now considering dynamical evolution from the given static state, where the excitation is initialized by a very short laser pulse, simulated as an instantaneous boost [42]. The question is to what extent the localization may be washed out through the excitation. In order to follow an evolution, one needs to characterize localization by one number and we do that by the spatial

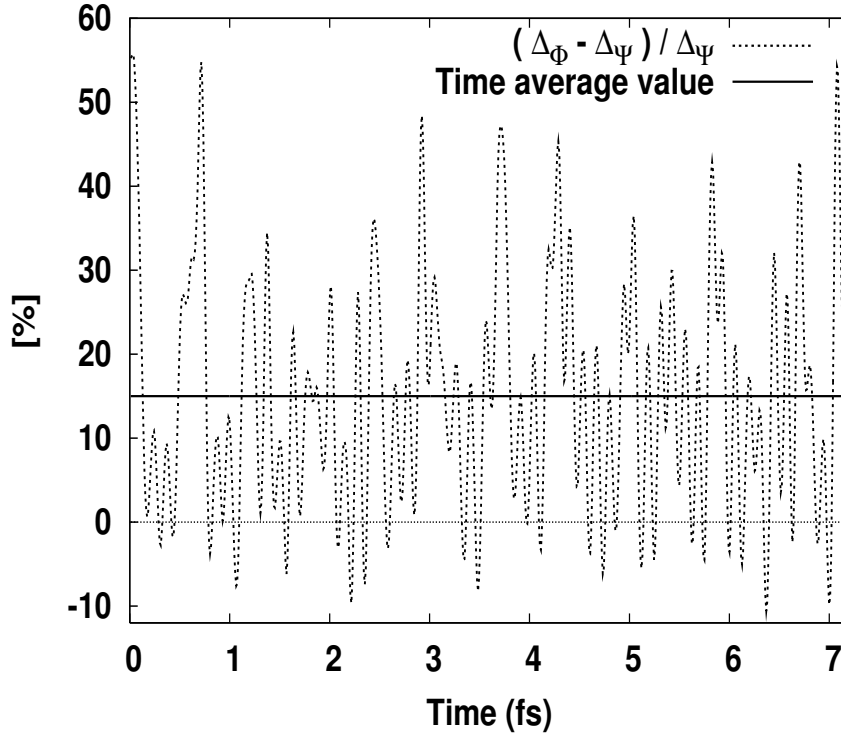


Fig. 3. Time evolution of single-particle variances (32) obtained in the 1D model with 2 electrons and asymmetrical ionic background. Shown is the relative value $(\Delta\varphi - \Delta\psi)/\Delta\psi$. The time averaged result is indicated by a straight line.

variance of a single particle states

$$\Delta\varphi = \sum_i (\varphi_i | x^2 | \varphi_i) - \left(\sum_i (\varphi_i | x^2 | \varphi_i) \right)^2 \quad (32)$$

and similarly for $\Delta\psi$, see Eq. (29). Fig. 3 shows the relative variance for the propagating state φ as compared to the localized state ψ (which was starting from the diagonal stationary state). The relative variance undergoes large fluctuations, as the variances as such do as well. But in the average, we see the expected result. The $\Delta\varphi$ remains larger than $\Delta\psi$, by about 15 % on time average.

6.2 Ionization properties

As a further observable, we consider the degree of ionization which, as stated above, is a sensitive quantity to probe the effect of SIC. Remind that absorbing bounds are applied for a proper handling of ionization. We use again an instantaneous boost to simulate a very short laser pulse. Fig. 4 shows the results for an atom of 3 electrons, within the 1D model and for two different initial boosts, comparing the TDHF benchmark with TDLDA and TDSIC.

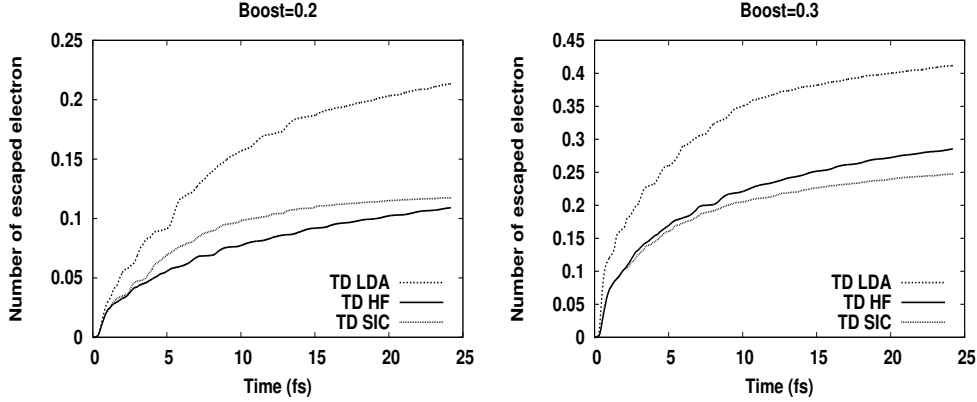


Fig. 4. Number of escaped electrons, as function of time, for an 1D atom of 3 electrons, initially excited by two different values of boost, as indicated. Three time-dependent schemes are compared : TDLDA, TDHF and TDSIC. The model parameters are $a = 0.5 a_0$, $b = 0.5 a_0$, $R = 0$, and $z = 0.5$.

The deposited energy with a boost of 0.2 / 0.3 Ha represents 60 % / 134 % of the LDA ionization energy (0.100 Ha) and 21 % / 47 % of the SIC ionization energy (0.133 Ha). Therefore we expect a strong ionization overestimation for LDA. It is obvious that TDSIC comes much closer to the benchmark (TDHF) than TDLDA. We checked various other 1D molecular systems and found similar results confirming that TDSIC recovers nicely the proper ionization features.

6.3 Results from 3D calculations

Finally, we want to check the effect of SIC in a realistic 3D situation. To that end, we consider the Na_5 cluster which has a non-symmetric planar structure (see insert in Fig. 6) and whose electron cloud is weakly bound and so provides a critical test case for formal developments [28]. This cluster contains altogether five valence electrons which are active in the low frequency irradiation processes. The core electrons of the Na atoms are much more bound and are eliminated by using pseudo-potentials. For the electronic exchange and correlations, we employ the energy-density functional of [39]. The laser excitation is again simulated by an instantaneous boost. For the further details of the 3D calculations see, e.g., [9,35]. The first principle result to be mentioned is that the newly developed solution scheme for TDSIC runs smoothly also for the full 3D case.

Fig. 5 compares the time evolution of ionization between TDLDA and TDSIC, for an initial boost of 0.125 Ha, whose deposited energy represents 149 % of the LDA ionization energy (0.105 Ha) and 90 % of the SIC ionization energy (0.172 Ha). We see a similarly dramatic effect from SIC on the ionization.

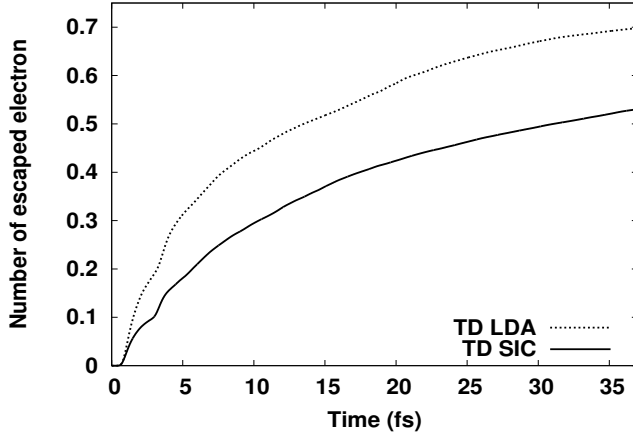


Fig. 5. Time evolution of the number electrons escaped from the Na_5 cluster, computed in full 3D. The system was initially excited by an instantaneous boost. TDSIC and TDLDA are compared.

TDSIC produces less in accordance with the fact that SIC enhances the IP from the LDA value of 0.105 Ha to the SIC value 0.172 Ha.

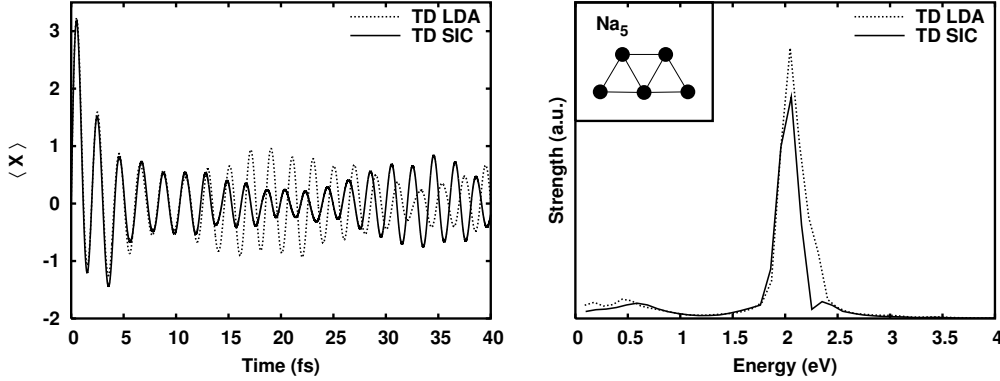


Fig. 6. Na_5 initially excited by an instantaneous boost and computed in full 3D, where TDSIC and TDLDA are compared. Left : Time evolution of the dipole spectra in x direction. Right : Optical absorption spectrum (in arbitrary units) derived thereof [42]; the insert shows the geometry of Na_5 .

Fig. 6 compares the time evolution of the dipole oscillation as such (left) and the subsequent optical response (right). The time evolution (left panel) shows that the initial oscillations are very much the same for TDLDA and TDSIC. Some deviations develop in the further course of propagation which emerges from different interferences with particle-hole states. This lets us expect that the Mie plasmon position is not affected by TDSIC, but that detailed fragmentation pattern may be different. These two features are indeed nicely found in the optical absorption spectra (right panel). Both results, reduced ionization together with little influence on the dominant Mie plasmon excitation was also found in earlier studies using a simplified SIC scheme, time-dependent average-density SIC [24,43].

While Na_5 is a soft system, as an alternative example of a strongly bound system, we consider the case of a C atom. The IP is now 0.224 Ha for LDA, whereas it is enhanced to 0.452 Ha for SIC. Then TDSIC produces much less ionization than TDLDA when the C atom is excited by an instantaneous boost, similarly to the case of Na_5 (see Fig. 5). We also compute the optical response spectrum for C, although this observable is less relevant for this non-metallic example than for Na_5 . We observe (not shown here) a shift between the SIC peak and the LDA peak. SIC also makes an effect on optical absorption because the deeper binding restricts the dipole oscillations more tightly than in case of LDA.

7 Conclusion

In that paper, we have investigated the time-dependent self-interaction correction method (TDSIC) which augments the time-dependent local-density approximation (TDLDA) by a self-interaction correction (SIC). That correction becomes crucial when aiming at the description of highly dynamical processes where electron emission plays a role. But SIC raises problems because the resulting one-body Hamiltonian becomes explicitly orbital dependent which, in turn, can destroy the necessary orthonormality of the single-particle states. One needs to add an explicit constraint on orthonormality. This leads to a “symmetry condition”, in other words, to the (plausible) condition that the SIC mean-field Hamiltonian is hermitian within the space of occupied states. An implementation of that involved condition in TDSIC has been achieved by dealing with two different sets of single-particle orbitals : Propagating orbitals which are carried forth by standard mean-field stepping methods and localizing (or SIC) orbitals which are used to compute the SIC mean-field. The relation between the two sets is established by a unitary transformation which is determined such that the localizing set satisfies the crucial symmetry condition at each time. The newly developed representation of TDSIC constitutes a formally consistent and numerically reliable scheme. Crucial conservation laws (energy, orthonormality, zero-force theorem) are all obeyed formally and in practical calculations.

First tests have been performed in a one-dimensional model for a molecule. By the standard rules of LDA, we have developed a LDA functional for exchange only. That allowed direct comparison with (time-dependent) Hartree-Fock (TDHF) as a benchmark. The dynamical evolution was initiated by exciting the ground state with a very short laser pulse. The pulse was idealized as an instantaneous boost and we computed for various excitation strengths to check the robustness of the results. It was found that TDSIC compares very well with TDHF, while TDLDA overestimates ionization by 50–100%. Tests had also been done for fully three dimensional calculations considering

a Na_5 molecule as test cases. We found again a substantial overestimation of ionization for TDLDA, in that case by about 30%.

Although full 3D calculations have proven to be feasible and stable, the TDSIC scheme is numerically costly. We consider it as a starting point for further developments towards more efficient schemes. The most costly detail is the fulfillment of the symmetry condition which basically provides more localized single-particle states. This suggests to replace the symmetry condition by a direct localization condition which will be numerically less costly. A promising option to find it is the time-dependent optimized effective potentials formalism [20,25]. It has already been used in the static case, leading to what we called a “Generalized Slater” potential [44]. The extension to the time dependent case is on the way.

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A Hermiticity of orthonormalization constraints

The constraint on orthonormality of the single-particle wavefunctions, or correspondingly unitarity of transformation coefficients, introduces a matrix of Lagrangian multipliers and that matrix ought to be hermitian. We prove that here for the case of the time-dependent variational principle (17). Let us split the matrix of Lagrange parameters λ into hermitian part μ and anti-hermitian part κ as $\lambda_{\gamma\beta} = \mu_{\gamma\beta} + \kappa_{\gamma\beta}$. The variational principle thus becomes $0 = \delta S$ for the action

$$S = \int_{t_0}^t dt' \left(\sum_{\alpha} (\psi_{\alpha} | i\hbar \partial_t | \psi_{\alpha}) - E_{\text{SIC}} + \sum_{\beta, \gamma} (\psi_{\beta} | \psi_{\gamma}) (\mu_{\gamma\beta} + \kappa_{\gamma\beta}) \right) . \quad (\text{A.1})$$

The action S subsequently splits into real and imaginary part where the latter reads simply

$$\Im\{S\} = \int_{t_0}^t dt' \sum_{\beta, \gamma} (\psi_{\beta} | \psi_{\gamma}) \kappa_{\gamma\beta} . \quad (\text{A.2})$$

Both parts are to be varied independently. Variation of the imaginary part yields

$$0 = \delta_{\psi_{\beta}^*} \Im\{S\} \implies \sum_{\gamma} \psi_{\gamma}(\mathbf{r}) \kappa_{\gamma\beta} = 0 \quad \forall \beta, \mathbf{r} \implies \kappa_{\gamma\beta} = 0 .$$

This means that we always have $\Im\{S\} = 0$ and we deal with a purely real action

$$S = \int_{t_0}^t dt' \left(\sum_{\alpha} (\psi_{\alpha} | i\hbar \partial_t | \psi_{\alpha}) - E_{\text{SIC}} + \sum_{\beta, \gamma} (\psi_{\beta} | \psi_{\gamma}) \lambda_{\gamma\beta} \right) , \quad \lambda_{\beta\gamma}^* = \lambda_{\gamma\beta} \quad (\text{A.3})$$

The same reasoning applies to all other form of action used for TDSIC paper and to the energy functional used for stationary SIC.

B Alternative derivations of TDSIC

In this appendix, we will present two alternative derivations of TDSIC. It is gratifying to see that different derivations all lead to the same result. The alternative routes also shed some new light on the intrinsic properties of TD-SIC.

B.1 The Goedecker method

First, we will use the Goedecker method of variation [17]. One starts from the SIC energy E_{SIC} as given in Eq. (4) and defined in term of the orthonormal set of single particle wavefunctions $\{\psi_\alpha\}$. Thanks to the Löwdin orthonormalization method [45], one could equally well expand the $\{\psi_\alpha\}$ into a set of non-orthogonal functions $\{\tilde{\psi}_\alpha\}$ as

$$\psi_\alpha = \sum_\beta s_{\beta,\alpha}^{-1/2} \tilde{\psi}_\beta \quad , \quad s_{\beta,\alpha} = (\tilde{\psi}_\beta | \tilde{\psi}_\alpha) \quad . \quad (\text{B.1})$$

This is actually another way to constrain the orthonormality of the $\{\psi_\alpha\}$. If one assumes that the $\{\tilde{\psi}_\alpha\}$ are not too far from orthonormality, one has to first order

$$\psi_\alpha \approx \sum_\beta (\delta_{\alpha\beta} - \sigma_{\alpha\beta}) \tilde{\psi}_\beta \quad , \quad \sigma_{\alpha\beta} = \frac{1}{2} (s_{\alpha\beta} - \delta_{\alpha\beta}) = \frac{1}{2} ((\tilde{\psi}_\beta | \tilde{\psi}_\alpha) - \delta_{\alpha\beta}) \quad (\text{B.2})$$

where $\sigma_{\alpha\beta}$ is a small quantity. One now applies the principle of stationary action when varying with respect to the $\tilde{\psi}_\alpha^*$ (the non-orthogonal functions). This yields

$$0 = \delta_{\tilde{\psi}_\alpha^*} \int_0^t dt' (\sum_\beta (\psi_\beta | i\hbar \partial_t \psi_\beta) - E_{\text{SIC}}) \quad . \quad (\text{B.3})$$

Using the chain rule for functional derivatives, we obtain

$$0 = \sum_\gamma \int d^3\mathbf{r}' \left(\frac{\delta\psi_\gamma(\mathbf{r}')}{\delta\tilde{\psi}_\alpha^*(\mathbf{r})} \frac{\delta}{\delta\psi_\gamma(\mathbf{r}')} + \frac{\delta\psi_\gamma^*(\mathbf{r}')}{\delta\tilde{\psi}_\alpha^*(\mathbf{r})} \frac{\delta}{\delta\psi_\gamma^*(\mathbf{r}')} \right) \left(\sum_\beta (\psi_\beta | i\hbar \partial_t \psi_\beta) - E_{\text{SIC}} \right) \quad .$$

The variations with respect to the orthonormal set $\delta\psi_\beta$ are similar to those used before in the derivations of TDSIC. Its evaluation yields

$$0 = \sum_\beta \int d^3\mathbf{r} \left\{ \frac{\delta\psi_\gamma^*(\mathbf{r})}{\delta\tilde{\psi}_\alpha^*(\mathbf{r})} \left(i\hbar \partial_t - \hat{h}_\gamma \right) \psi_\gamma - \psi_\gamma^* \left(i\hbar \overleftarrow{\partial}_t + \hat{h}_\gamma \right) \frac{\delta\psi_\gamma(\mathbf{r})}{\delta\tilde{\psi}_\alpha^*(\mathbf{r})} \right\} \quad .$$

The crucial step is now to evaluate the $\delta\tilde{\psi}_\alpha^*$ derivatives. Using Eq. (B.2) and taking into account that $\delta\tilde{\psi}_\alpha^*$ appears not only explicitly in the expansion, but also implicitly in the coefficients $\sigma_{\alpha\beta}$, yields

$$\frac{\delta\psi_\beta^*(\mathbf{r})}{\delta\tilde{\psi}_\alpha^*(\mathbf{r}')} = \delta^3(\mathbf{r}-\mathbf{r}') [\delta_{\alpha\beta} - \sigma_{\alpha\beta}] - \frac{1}{2} \sum_k \psi_k(\mathbf{r}') \tilde{\psi}_k^*(\mathbf{r}) \delta_{\alpha\beta} ,$$

$$\frac{\delta\psi_\beta(\mathbf{r})}{\delta\tilde{\psi}_\alpha^*(\mathbf{r}')} = -\frac{1}{2} \tilde{\psi}_\alpha(\mathbf{r}) \psi_\beta(\mathbf{r}') .$$

Note that we can let $\sigma_{\alpha\beta} \longrightarrow 0$ after variation. Thus we obtain finally the TDSIC equation

$$0 = (i\hbar\partial_t - \hat{h}_\alpha)|\psi_\alpha\rangle - \sum_\beta |\psi_\beta\rangle(\psi_\beta|i\hbar\partial_t - \frac{\hat{h}_\alpha + \hat{h}_\beta}{2}|\psi_\alpha\rangle \quad (\text{B.4})$$

The symmetry condition is recovered by projecting Eq. (B.4) on $(\psi_\beta|$.

B.2 Unitary variation

Section B.1 uses a variation where orthonormality is explicitly obeyed which allows to work without Lagrangian parameters. There is an interesting alternative for such a technique. One deals with a unitary variation according to Thouless theorem [46]. Any variation from one Slater state $|\Phi\rangle$ to another Slater state $|\Phi'\rangle$ can be expressed as

$$|\Phi'\rangle = \exp(i\hat{A})|\Phi\rangle \quad , \quad \hat{A}^\dagger = \hat{A} \quad . \quad (\text{B.5a})$$

A variation is a small change and thus the varied states can be obtained from linearization. This means

$$|\delta\Phi\rangle = i\hat{A}|\Phi\rangle \quad , \quad \langle\delta\Phi| = -i\langle\Phi|\hat{A}^\dagger = -i\langle\Phi|\hat{A} \quad , \quad (\text{B.5b})$$

and subsequently in terms of single-particle wavefunctions

$$|\delta\psi_\alpha\rangle = i \sum_{n=1}^{\infty} |\delta\psi_n\rangle A_{n\alpha} = i \sum_{\beta \in \text{occ}} |\delta\psi_\beta\rangle A_{\beta\alpha} + i\hat{A}_\perp |\delta\psi_\alpha\rangle \quad , \quad (\text{B.5c})$$

$$\langle\delta\psi_\alpha| = -i \sum_{n=1}^{\infty} A_{\alpha n} \langle\delta\psi_n| = -i \sum_{\beta \in \text{occ}} A_{\alpha\beta} \langle\delta\psi_\beta| - i\langle\delta\psi_\alpha|\hat{A}_\perp \quad , \quad (\text{B.5d})$$

$$\hat{A}_\perp = \hat{A}\hat{\Pi}_\perp + \hat{\Pi}_\perp\hat{A} \quad , \quad (\text{B.5e})$$

where one should be aware of the different ranges of summations, the n running over all single-particle space and the β only of occupied states. The operator \hat{A}_\perp is the part of the operator leading into space orthogonal to the occupied states. Variation then corresponds to a free variation of the matrix elements of the hermitian operator \hat{A} (as long as hermiticity is obeyed). However, the limitation to hermiticity means that $|\delta\psi_\alpha\rangle$ and $\langle\delta\psi_\alpha|$ cannot be varied independently anymore.

Applying that variation to the principle of stationary action yields

$$\begin{aligned}
0 &= \sum_{\beta \in \text{occ}} \left\{ -i(\psi_\beta | \hat{A} (\hat{h} \partial_t - \hat{h}_\beta) | \psi_\beta) - i(\psi_\beta | (\hat{h} \overleftarrow{\partial}_t + \hat{h}_\beta) \hat{A} | \psi_\beta) \right\} \\
&= \sum_{\beta \in \text{occ}} \sum_{n=1}^{\infty} \left\{ -iA_{\beta n}(\psi_n | (\hat{h} \partial_t - \hat{h}_\beta) | \psi_\beta) - i(\psi_\beta | (\hat{h} \overleftarrow{\partial}_t + \hat{h}_\beta) | \psi_n) A_{n\beta} \right\} \\
&= \sum_{\beta \in \text{occ}} \sum_{n \perp \text{occ}} \left\{ -iA_{\beta n}(\psi_n | (\hat{h} \partial_t - \hat{h}_\beta) | \psi_\beta) - i(\psi_\beta | (\hat{h} \overleftarrow{\partial}_t + \hat{h}_\beta) | \psi_n) A_{n\beta} \right\} \\
&\quad - i \sum_{\beta \in \text{occ}} A_{\beta\alpha}(\psi_\alpha | (\hat{h} \partial_t - \hat{h}_\beta) | \psi_\beta) - i \underbrace{\sum_{\beta \in \text{occ}} (\psi_\beta | (\hat{h} \overleftarrow{\partial}_t + \hat{h}_\beta) | \psi_\alpha) A_{\alpha\beta}}_{i \sum_{\beta \in \text{occ}} (\psi_\alpha | (\hat{h} \partial_t + \hat{h}_\alpha) | \psi_\beta) A_{\beta\alpha}} \\
&= \sum_{\beta \in \text{occ}} \sum_{n \perp \text{occ}} \left\{ -iA_{\beta n}(\psi_n | (\hat{h} \partial_t - \hat{h}_\beta) | \psi_\beta) - i(\psi_\beta | (\hat{h} \overleftarrow{\partial}_t + \hat{h}_\beta) | \psi_n) A_{n\beta} \right\} \\
&\quad + i \sum_{\beta \in \text{occ}} A_{\beta\alpha}(\psi_\alpha | \hat{h}_\beta - \hat{h}_\alpha | \psi_\beta) \quad .
\end{aligned}$$

Now, the matrix elements $A_{\beta n}$ and $A_{n\beta}$ can be varied independently because $A_{n\beta} = A_{\beta n}^* \in \mathbb{C}$. Similarly, all elements $A_{\beta\alpha}$ can be considered as being independent. This yields the TDSIC equations as

$$\hat{\Pi}_\perp i\hbar \partial_t \psi_\alpha = \hat{\Pi}_\perp \hat{h}_\alpha \psi_\alpha \quad , \quad (\text{B.6a})$$

$$0 = K_{\alpha\beta} \quad . \quad (\text{B.6b})$$

That, again, reproduces the TDSIC equations (after proper rewriting) together with the symmetry condition.

C LDA exchange energy of the 1D model

One has to evaluate the exchange-correlation energy as a functional of the local one-body density :

$$E_{\text{XC}}[\rho] = \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' (\Gamma(\mathbf{r}, \mathbf{r}') - \rho(\mathbf{r})\rho(\mathbf{r}')) \langle \mathbf{r} | \hat{v} | \mathbf{r}' \rangle \quad (\text{C.1})$$

For fermionic systems, in the general case :

$$\Gamma(\mathbf{r}, \mathbf{r}') = \langle \psi | \hat{\Gamma}(\mathbf{r}, \mathbf{r}') | \psi \rangle \quad (\text{C.2})$$

where $\hat{\Gamma}(\mathbf{r}, \mathbf{r}') = \sum_{i>j} \{ \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) + \delta(\mathbf{r} - \mathbf{r}_j) \delta(\mathbf{r}' - \mathbf{r}_i) \}$ is the local two-body density matrix (which Pauli effects are included in). In the following, we

will focus on the exchange energy only, so that we can limit the ψ to Slater determinants.

In the 1D model, one now has to compute :

$$\Gamma(x, x') = \frac{1}{2} \sum_{i,j} \langle ij | \hat{\Gamma}(x, x') | \tilde{ij} \rangle, \quad (\text{C.3})$$

with :

$$\hat{\Gamma}(x, x') = \sum_{i>j} \{ \delta(x - x_i) \delta(x' - x_j) + \delta(x - x_j) \delta(x' - x_i) \} \quad (\text{C.4})$$

For a 1D free gas, \sum_i becomes $\int dk_i \frac{\gamma L}{2\pi}$ (where L is the length of the box) and $\langle ij | \hat{\Gamma}(x, x') | \tilde{ij} \rangle = \frac{2}{L^2} \left\{ 1 - \frac{1}{\gamma} \cos[(k_i - k_j)(x - x')] \right\}$. Inserting this in Eq. (C.3), one gets :

$$\Gamma(x, x') = \left(\frac{\gamma}{2\pi} \right)^2 \int dk_i dk_j \left[1 - \frac{1}{\gamma} \Re \left(e^{i(k_i - k_j)(x - x')} \right) \right] \quad (\text{C.5})$$

The first part of the integral gives k_F^2 ; the other part is proportional to :

$$\int dk_i e^{ik_i(x-x')} \int dk_j e^{-ik_j(x-x')} = \frac{e^{ik_F(x-x')} - 1}{i(x-x')} \times \frac{e^{-ik_F(x-x')} - 1}{-i(x-x')} = 2 \frac{1 - \cos[k_F(x-x')]}{(x-x')^2} \quad (\text{C.6})$$

Collecting these results in (C.5), one finds :

$$\Gamma(x, x') = \rho_0^2 \left\{ 1 - \frac{2}{\gamma} D[k_F(x - x')] \right\} \quad (\text{C.7})$$

with the 1D free gas density, $\rho_0 = \frac{\gamma k_F}{2\pi}$, and $D(x) = \frac{1 - \cos x}{x^2}$.

We now insert (C.7) in the 1D version of (C.1). If the 1D potential is a smoothed Coulomb one, such as $\frac{1}{\sqrt{(x-x')^2 + a}}$ (in Hartree units), a straightforward change of variable gives :

$$\rho \varepsilon_X(\rho) = -\frac{\rho_0^2}{\gamma} \int_{-\infty}^{+\infty} dx \frac{D(k_F x)}{\sqrt{x^2 + a}} = -\frac{\gamma}{(2\pi)^2} \int_{-\infty}^{+\infty} dx \frac{1 - \cos(\frac{2\pi\rho_0}{\gamma} x)}{x^2 \sqrt{x^2 + a}}. \quad (\text{C.8})$$

The LDA exchange potential then reads :

$$U_{\text{LDA}}^X[\varrho] = \frac{\delta}{\delta \rho} (\rho \varepsilon_X(\rho))|_{\rho=\varrho} = -\frac{1}{2\pi} \int_{-\infty}^{+\infty} dx \frac{\sin(\frac{2\pi\varrho}{\gamma} x)}{x \sqrt{x^2 + a}} \quad (\text{C.9})$$

D Proof of the conservation laws

D.1 Energy conservation

The proof of energy conservation is straightforward and does not need any comments :

$$\begin{aligned}
\partial_t E_{\text{SIC}} &= \int d^3\mathbf{r} \sum_i \partial_t \varphi_i^*(\mathbf{r}, t) \frac{\delta E_{\text{SIC}}}{\delta \varphi_i^*(\mathbf{r}, t)} + \text{c.c.} \\
&= \sum_i (\partial_t \varphi_i | \hat{h}_{\text{SIC}} \varphi_i) + \sum_i (\hat{h}_{\text{SIC}} \varphi_i | \partial_t \varphi_i) \\
&= -i \sum_i (\hat{h}_{\text{SIC}} \varphi_i | \hat{h}_{\text{SIC}} \varphi_i) + i \sum_i (\hat{h}_{\text{SIC}} \varphi_i | \hat{h}_{\text{SIC}} \varphi_i) = 0 \quad .
\end{aligned}$$

D.2 Orthonormality conservation

The orthonormality should be conserved during time propagation because we imposed it in the variation of the action. Nevertheless we will check it explicitly. Using the TDSIC resulting propagation scheme (31), we see that a sufficient condition for the orthonormality to be conserved is that the propagator is unitary within the space of occupied states, i.e.,

$$(\varphi_i | e^{-i\hat{h}_{\text{SIC}}} | \varphi_j) = (\varphi_j | e^{-i\hat{h}_{\text{SIC}}} | \varphi_i)^* \quad . \quad (\text{D.1})$$

This last equation is obviously verified in the occupied subspace (only), because of the "weak" hermiticity of \hat{h}_{SIC} in this subspace as given by the symmetry condition (10c).

D.3 Zero-Force Theorem

The Zero-Force Theorem (ZFT) states that the kinetic energy plus the electron-electron interaction part in the Kohn-Sham mean-field do not change the total momentum of the electron cloud which is due to translational symmetry of the electron-electron interaction and of the kinetic energy. We formulate that symbolically as $\partial_t^{(\text{kin,el})} \langle \mathbf{p} \rangle = 0$. The proof starts from the Kohn-Sham equations where all external fields are dropped

$$\left(\frac{\mathbf{p}^2}{2m} + \hat{U}^{(\text{el})} \right) |\varphi_i\rangle = i\hbar \partial_t^{(\text{kin,el})} |\varphi_i\rangle \quad , \quad (\text{D.2})$$

and where $\hat{U}^{(\text{el})}$ is the Kohn-Sham mean-field part stemming from the electrons. The time change of total momentum reads

$$\begin{aligned}
\partial_t^{(\text{kin,el})} \sum_i (\varphi_i | \mathbf{p} | \varphi_i) &= \sum_i \left[(\partial_t^{(\text{kin,el})} \varphi_i | \mathbf{p} | \varphi_i) + (\varphi_i | \mathbf{p} | \partial_t^{(\text{kin,el})} \varphi_i) \right] \\
&= \sum_i \left[(\partial_t^{(\text{kin,el})} \varphi_i | \mathbf{p} \varphi_i) + (\mathbf{p} \varphi_i | \partial_t^{(\text{kin,el})} \varphi_i) \right] \\
&= \frac{1}{i\hbar} \sum_i \left[-(U^{(\text{el})} \varphi_i | \mathbf{p} \varphi_i) + (\mathbf{p} \varphi_i | U^{(\text{el})} \varphi_i) \right] \quad (\text{D.3})
\end{aligned}$$

The general form of the ZFT is thus, in $\{\mathbf{r}\}$ representation

$$\sum_i \int d^3\mathbf{r} \left[(\mathbf{r} | U^{(\text{el})} | \varphi_i)^* \nabla \varphi_i(\mathbf{r}) + (\mathbf{r} | U^{(\text{el})} | \varphi_i) \nabla \varphi_i^*(\mathbf{r}) \right] = 0 \quad (\text{D.4})$$

Now we check whether the TDSIC equation fulfills this theorem, where $(\mathbf{r} | U^{(\text{el})} | \varphi_i) = \sum_\alpha u_{i\alpha}^* \psi_\alpha U_{\text{LDA,el}}[|\psi_\alpha|^2]$. After simple manipulations on (D.4), one obtains :

$$\begin{aligned}
\sum_i \int d^3\mathbf{r} \left[(\mathbf{r} | U^{(\text{el})} | \varphi_i)^* \nabla \varphi_i(\mathbf{r}) + (\mathbf{r} | U^{(\text{el})} | \varphi_i) \nabla \varphi_i^*(\mathbf{r}) \right] \\
= \sum_\alpha \int d^3\mathbf{r} U_{\text{LDA,el}}[|\psi_\alpha|^2] \nabla |\psi_\alpha|^2 \\
= \sum_\alpha \int d^3\mathbf{r} U_\alpha \nabla \rho_\alpha \quad (\text{D.5})
\end{aligned}$$

in compact notations. However, since U_α is obtained variationally, we have :

$$\begin{aligned}
\int d^3\mathbf{r} U_\alpha \nabla \rho_\alpha &= \int d^3\mathbf{r} d^3\mathbf{r}' \frac{\delta E}{\delta \rho_\alpha(\mathbf{r})} \frac{\delta \rho_\alpha(\mathbf{r})}{\delta \mathbf{r}'} \\
&= \int d^3\mathbf{r}' \frac{\delta E}{\delta \mathbf{r}'} \\
&= 0 \quad (\text{D.6})
\end{aligned}$$

As a consequence, TDSIC does verify the ZFT relation (D.4), as any variational scheme should.

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